REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	3/29/2001	Final ~~Technical~~ Report (05/01/96 – 10/31/00)

4. TITLE AND SUBTITLE
Electronic Bottleneck and Coherent Vibrational Effects on the Relaxation Dynamics of Photoexcited Ions in Crystals

5. FUNDING NUMBERS
DAAH04-96-1-0071 ~~(RF 47365)~~

6. AUTHOR(S)
P.I. - R. R. Alfano
Researchers – Dr. W. B. Wang, Ms. C. H. Liu, Mr. S. Owen

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
City College of New York,
Convent Avenue at 138th Street,
New York, NY 10031

8. PERFORMING ORGANIZATION REPORT NUMBER
ARO 35578.2-PH-SAH

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U. S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT	12 b. DISTRIBUTION CODE
Approved for public release; distribution unlimited.	

13. ABSTRACT (Maximum 200 words)

Nonradiative relaxation processes of photoexcited impurity ions in Cr^{4+}-doped forsterite (Cr^{4+}:Mg_2SiO_4) and Cunyite (Cr^{4+}:Ca_2GeO_4) laser crystals have been investigated using time-resolved resonance Raman and up-converted hot luminescence spectroscopy methods. The nonequilibruim population of a local mode of 765 cm^{-1} in Cr^{4+}:Mg_2SiO_4 was found to build up during the transition through an electronic bottleneck and decay by interaction with a restricted number of phonon modes. The resonance energy transfer from a local mode of 733 cm^{-1} in Cr^{4+}:Ca_2GeO_4 to resonance phonon mode of the host crystal was found to dominate the initial step of the energy relaxation of the photoexcited impurity ions. Our work has gained a better understanding of the electronic-vibronic nonradiative relaxation processes which is of great importance for optical and lasing properties of solid state tunable crystals.

14. SUBJECT TE	15. NUMBER OF PAGES
Prof. R. R. Alfano, Dr. W. B. Wang, Ms. C. H. Liu, Mr. S. Owen, Dr. D. M. Calistru, and Dr. S. G. Demos	15
	16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION ON THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

FINAL PROGRESS REPORT

For ARO Grant DAAH 04-96-1-0071 (CUNY RF 47365)

Entitled "Electronic bottleneck and coherent vibrational effect on relaxation dynamics of photoexcited ions in crystals"

Period Covered: 05/01/96 – 10/31/00

Table of Contents

---

1. Statement of the Problem Studied

The subject studied in this project is the vibronic and electronic dynamics of a tetravalent chromium (Cr^{4+}) ion, an important laser-active ion for the near-infrared spectral region, in various host crystals using Raman and time-resolved laser spectroscopy methods. This work is needed to gain a better and more fundamental understanding of the electronic bottlenecks and the vibronic nonradiative relaxation processes which affect both optical and lasing properties of solid state tunable crystals.

2. Summary of the Most Important Results:

We have investigated the nonradiative relaxation processes in Cr^{4+}-doped forsterite ($Cr^{4+}:Mg_2SiO_4$) and Cunyite ($Cr^{4+}:Ca_2GeO_4$) laser crystals using Raman and time-resolved laser spectroscopy methods. The time-resolved resonance Raman measurement of dynamics of photoexcited impurity ions during nonradiative relaxation for $Cr^{4+}:Mg_2SiO_4$ laser crystal has been performed, and the decay processes from a local mode (impurity associated) to a phonon mode (lattice associated) have been investigated. A theoretical model governing the nonradiative energy transfer from a photoexcited impurity ion into a host lattice in a Cr^{4+}-doped laser crystal has been studied. The up-converted hot luminescence measurement of dynamics of photoexcited ions in $Cr^{4+}:Ca_2GeO_4$ laser crystal has been performed to investigate the resonance energy transfer from a local mode to a phonon mode.

The important results obtained from this research project have been reported to ARO, and published in scientific journals including Physical Review Letters.

The following summarizes our results:

2(a) Time-resolved resonance Raman measurement of dynamics of a local mode during nonradiative relaxation for forsterite ($Cr^{4+}:Mg_2SiO_4$)

The energy transfer from a local mode to a phonon mode during the nonradiative relaxation processes taking place in an impurity-doped laser crystal was first experimentally studied in $Cr^{4+}:Mg_2SiO_4$ by investigating the dynamics of the 765 cm^{-1} Cr^{4+} local mode using time-resolved resonance Raman scattering.[1]

The sample selected for investigation was 10 x 8 x 6 mm^3 oriented $Cr^{4+}:Mg_2SiO_4$ single crystal. Mg_2SiO_4 belongs to the olivine family with lattice constants of a=10.22 A, b=5.99 A, and c=4.76 A. Cr^{4+} substitutes for Si^{4+} in a tetrahedrally distorted position.[2]

Fig.1 shows the anti-Stokes resonance Raman spectra for Cr^{4+}-doped Mg_2SiO_4 laser crystal and Raman Ag spectra for undoped Mg_2SiO_4 host crystal in the 500-900 cm^{-1} spectral range obtained using our photon counting image acquisition system (PIAS, Hamamatsu Model C18150) with a SPEX triplemate spectrograph under the excitation wavelength of 598 nm.[3] The salient feature is the appearance of 765 cm^{-1} Cr^{4+} local mode in the resonance Raman spectrum, which has highest scattering cross-section and is selected to investigate the dynamics of the local mode using time-resolved resonance Raman spectroscopy.

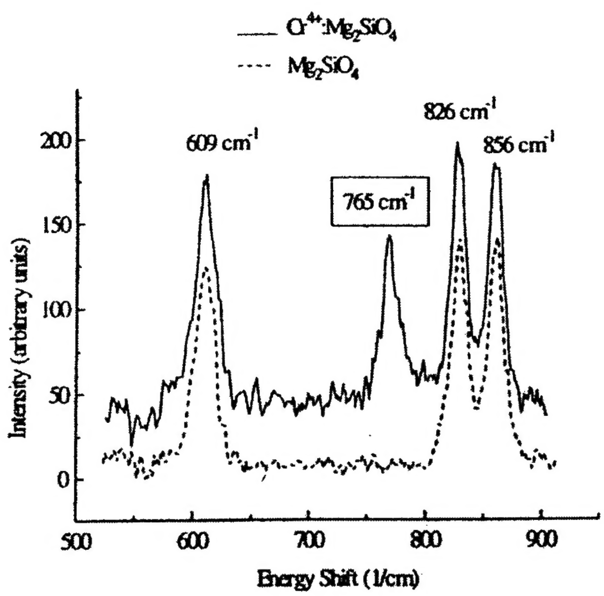

Fig.1 Anti-Stokes resonance Raman (continuous line) and Raman (dashed line) Ag spectra for Cr^{4+}:Mg_2SiO_4 laser crystal and undoped Mg_2SiO_4 host crystal, respectively, obtained under 598 nm excitation, in the 500-900 cm^{-1} spectral range. The 765 cm^{-1} Cr^{4+} local mode is boxed.[3]

In the time-resolved Raman measurement, Cr^{4+} ions were excited near the zero-phonon line of the $^3B_2$ ($^3T_1$) state with 500 fs linearly polarized 598 nm pulses, corresponding to the maximum anti-Stokes resonance enhancement for the 765 cm^{-1} Cr^{4+} local mode. The excitation pulses were obtained from a Rh-6G dye laser synchronously pumped by a mode-locked Nd:YAG laser. The dynamics of the local mode was investigated using pump-probe setup by time delaying the probe beam of the same

wavelength as the pump and monitoring the relative changes in the anti-Stokes signal for the local mode for different time delays. In addition, the dynamics of the 335 cm^{-1} daughter phonon mode involved in the most probable decay pathway of the 765 cm^{-1} local mode was also investigated.[1]

The measured normalized relative change in the integrated intensity of the 765 cm^{-1} local mode for different time delays, and the measured dynamics of the 335 cm^{-1} daughter phonon mode are shown in Fig.2. No information was obtained on the dynamics of the 424 cm^{-1} daughter phonon mode because it is too weak to be resolved in an anti-Stokes Raman spectrum.

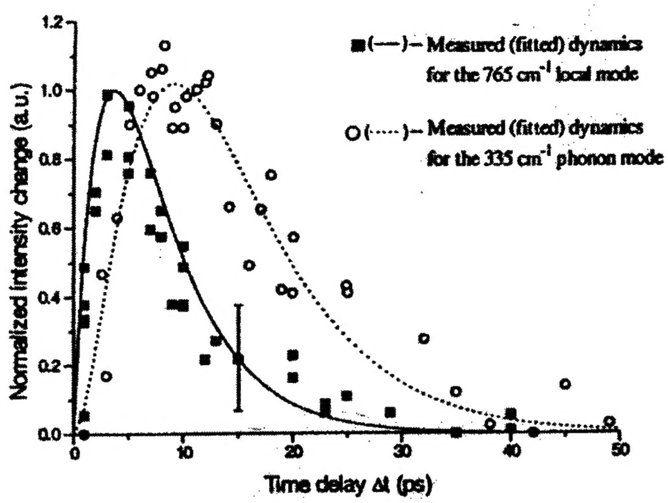

Fig.2 Normalized measured and fitted relative change in the integrated intensity of the 765 cm^{-1} local mode and the 335 cm^{-1} daughter mode for different time delays.[1]

The temporal profiles in Fig.2 show that the nonequilibrium 765 cm^{-1} local mode population builds up during the initial 3-4 ps while the nonequilibrium 335 cm^{-1} daughter phonon mode population reaches its maximum ~8 ps following photoexcitation. It is clear that the 335 cm^{-1} daughter phonon is created during the decay of the 765 cm^{-1} local mode, which gives a time-shifted temporal for nonequilibrium daughter phonons.

This measured dynamics indicates that the nonradiative relaxation proceeds via transfer of the nonequilibrium local mode population generated during the transition through an electronic bottleneck, to a select number of daughter phonons rather than through direct interaction with the phonon continuum (see Fig.3).

2(b) Investigation of nonradiative relaxation pathway of photoexcited impurity ions

In order to explain the time-resolved Raman experimental data, a dynamics model shown in Fig.3 was developed. The 598 nm pump pulse photoexcites Cr^{4+} ions near the zero-phonon line of the $^3B_2(^3T_1)$ state, creating an excited state population $\eta(t)$. The lack of emission from the $^3B_2(^3T_1)$ state suggests that Cr^{4+} ions relax nonradiatively towards the metastable level at 9150 nm, by making a transition to the lower lying ^1E state. Since this transition is spin forbidden, the system requires a longer tunneling time, giving rise to an electronic bottleneck. The presence of the $^3B_2(^3T_1)$- ^1E bottleneck was first reported using the up-converted hot luminescence technique, and its lifetime was measured to be ~10 ps.[4] As the electronic transition is accompanied by an increase in the occupation number for local modes [electronic-vibronic transitions as shown in Fig.3(a)], it is expected that the nonequilibrium local mode population rises during the time needed to cross the electronic bottleneck.

Following the transition through the electronic bottleneck, the local mode population decays nonradiatively. The energy of the nonequilibrium local mode population can be transferred nonradiatively into the lattice by one of the following processes: the local mode interacts with the lattice represented by a continuum of phonon modes and distributes the excess energy into the reservoir, and/or the local mode interacts with a very restricted number of vibrations (daughters) which take over the excess energy and display a transient, "time-shifted" (from the driving local mode) nonequilibrium population. The most likely energetic-wise daughter decay channels for the investigated 765 cm^{-1} local mode is decay into two phonon modes, such that 765 $cm^{-1} \rightarrow$ 335 cm^{-1} + 424 cm^{-1}. As the nonequilibrium mother local mode population decreases, the nonequilibrium daughter phonon mode which are driven by this particular decay route increase. The nonequilibrium daughter phonon mode population then decays by interactions with the phonon continuum allowing the system to return to thermal equilibrium.

Since there is no phonon mode in resonance with the 765 cm^{-1} local mode as shown in Fig.1, resonance nonradiative processes directly from local mode to resonance phonon mode can not occur for the 765 cm^{-1} local mode.

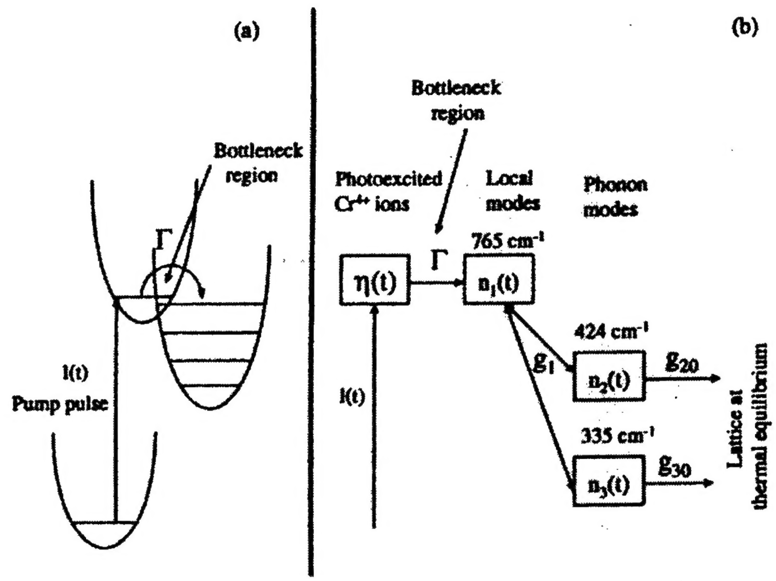

Fig.3 (a) Schematic diagram indicating the increase in the local mode population following the crossing of the $^3B_2$ ($^3T_1$) $\rightarrow$ ^1E electronic bottleneck, and (b) the intermolecular nonradiative relaxation pathway for the 765 cm^{-1} local mode and characteristic decay rates.[1]

The intermolecular nonradiative decay pathway can be modeled using the scheme indicated in Fig.3(b). The equations describing the dynamics of the ion-lattice system can be solved exactly for a δ-shaped laser pulse. The best fitting shown in Fig.2 generates the following key parameters: $^3B_2$ ($^3T_1$) $\rightarrow$ ^1E electronic bottleneck transition time 2.8 ± 0.3 ps, local mode lifetime (due only to an intermolecular anharmornic decay channel) 5.1 ± 0.5 ps, birth time of daughter phonons 7.9 ± 0.6 ps, and lifetime of daughter phonons (due to interaction with the continuum of phonons) 5 ± 0.5 ps.

2(c) Theoretical study of nonradiative energy transfer from impurity ions into a host lattice for Cr^{4+}-doped laser crystals

We have studied and developed a theoretical model explaining the nonradiative energy transfer from a photoexcited impurity ion into a host lattice in a laser crystal.[5] The energy-transfer mechanism consists of electronic energy transfer to local vibrations that then dissipate their energy to lattice (phonon) modes of the same energy creating a nonequilibrium phonon population. The model explains the experimental temporal

profiles of nonequilibrium optical phonons probed by time-resolved Raman scattering in Cr^{4+}-doped forsterite laser crystal shown in Fig.2. The electronic transition time and relaxation lifetimes for phonon and local modes are ~3, 4 and 8 ps, respectively, which are in good agreement with our measured values obtained from the time-resolved Raman experiment.

2(d) Up-converted hot luminescence measurements of energy transfer from a local mode to a phonon mode in the Cunyite ($Cr^{4+}:Ca_2GeO_4$)

The up-converted hot luminescence in highly efficient tunable Cunyite ($Cr^{4+}:Ca_2GeO_4$) laser crystal was measured and used to investigate the relaxation dynamics of photoexcited ions in laser crystals. The resonance energy transfer from a local mode of the impurity ions into a phonon mode of the host crystal lattice was found to dominate the initial step of energy relaxation of photoexcited impurity ions.[6]

The laser crystal under investigation is a heavily doped 3 x 5 x 7 mm^3 $Cr^{4+}:Ca_2GeO_4$ single crystal grown by a top-seeded solution growth method and containing 0.3 Cr^{4+} at % wt. The Cunyite crystal belongs to the olivine family with lattice constants of a = 11.4 Å, b = 6.79 Å and c = 5.24 Å.

Polarized absorption and emission spectra identified the tetrahedrally coordinated Cr^{4+} as the only optically active center[7] (while $Cr:Mg_2SiO_4$ has both Cr^{3+} and Cr^{4+} active centers). The room temperature absorption spectrum of the sample for E || c axis shows an absorption peak at 620 nm corresponding to $^3A_2 \rightarrow {}^3B_2\,(^3T_1)$ dipole allowed transition. The near infrared fluorescence spectra of $Cr^{4+}:Ca_2GeO_4$ shows that the metastable level of Cunyite is located at E_{ML} = 1.043 ev (1189 nm) [7]

The up-converted hot luminescence technique utilizes a two-step excitation process.[4] In the first step, the pump photons excite the impurity ions to an upper electronic state situated above the metastable level (E_{ML}). In the second step, the photoexcited ions relax to the bottom of the metastable level, absorb another pump photon (E_{photon}), and reach a higher excited energy level (E_{EL}). This process satisfies the energy equation of $E_{EL} = E_{photon} + E_{ML}$. Subsequent to these two-step photoexcitations, radiative and nonradiative relaxation occurs and impurity ion local modes are populated. Emission arising from radiative transitions from the short-lived local modes to the ground electronic state of ions at different step of energy relaxation forms a number of hot luminescence peaks. The

energy separation between successive peaks in the up-converted hot luminescence spectra reveals the initial steps of nonradiative energy transfer from the impurity ion into the lattice allowing for identification of the participating phonon modes.

The measured up-converted hot luminescence spectra obtained under excitation wavelengths of 598 nm and 588 nm shows that energy separation between successive peaks is 726 ± 25 cm^{-1}. This energy coincides with the energy of the phonon mode of $E_{phonon} = 733$ cm^{-1} in resonance with a local mode of the impurity ions obtained by Raman measurements.[6, 8] Our up-converted hot luminescence indicates that the resonant energy transfer from the local mode of the excited impurity ions to the resonance phonon mode of the host crystal marked by $\omega_L \rightarrow \omega_p$ dominates the initial step of the energy relaxation of the photoexcited impurity ions. The energy of the photoexcited ions is first transferred from a local mode into a resonant phonon mode. The phonon mode then undergoes nonradiative decay by interacting with the phonon continuum bath, which dissipates the excess energy into the lattice and allows the system to return to thermal equilibrium.

In summary, we have experimentally and theoretically investigated the dynamics of local and phonon modes during the electronic-vibronic nonradiative relaxatrion of a photoexcited laser impurity ion proving the active participation of local modes in the nonradiative relaxation processes. We have shown that the nonequlibrium local mode population builds up during the transition through an electronic bottleneck and decays by interaction with a restricted number of phonon modes. We have also shown that the resonant energy transfer from the local mode of the excited impurity ions to the resonance phonon mode of the host crystal dominates the initial step of the energy relaxation of the photoexcited impurity ions.

Nonradiative relaxation processes significantly alters the room temperature operation of impurity doped solid state lasers, especially in the near- and mid-IR spectral regions. Our work has gained a better understanding of the electronic-vibronic nonradiative relaxation processes which is of great importance for lasing properties of solid state tunable crystals. We have produced several new Cr^{4+}-doped laser materials as an out growth of this program, in particular, Cunyite.

3. Publications and Presentations Under the Support of the Grant

1. Dana M. Calistru, S. G. Demos, and R. R. Alfano, "Dynamics of local modes during nonradiative relaxation", Phys. Rev. Lett., 78, 374 (1997).
2. V. A. Kremerman, M. Lax, S. G. Demos, Dana M. Calistru, and R. R. Alfano, " Nonradiative energy transfer from the impurity ion into the host lattice for Cr^{4+} - doped forsterite laser crystal" , Phys. Rev. B56, 14391 (1997-II).
3. J. M. Evans, V. Petricevic, A. B. Bykov, A. Delgado, and R. R. Alfano, "Direct diode-pumped continuous-wave near-infrared tunable laser operation of Cr^{4+}: forsterite and Cr^{4+}: Ca_2GeO_4", Opt. Lett. 22, 1171 (1997).
4. Dana M. Calistru, S. G. Demos, Scott Owen, V. Petricevic, and R. R. Alfano, "Role of local-phonon mode coupling in the nonradiative relaxation for designing more efficient impurity doped solid state laser crystals", OSA TOPS, Vol. 10, "Advance Solid State Lasers", edited by C. R. Pollock and W. R. Bosenberg, pp 435-439 (1997).
5. Scott Owen, S. G. Demos, Dana M. Calistru, V. Petricevic, and R. R. Alfano, "The resonance between local and phonon modes in Cr^{4+}: Ca_2GeO_4 Promotes nonradiative energy transfer", presented at the OSA 1997 Annual Meeting, Long Beach, California, October 12-17, 1997.
6. Dana M. Calistru, S. G. Demos, and R. R. Alfano, "Role of intra- inter-molecular and resonance decay pathway in nonradiative processes taking place in impurity doped solid state laser crystals", presented at the 14th International laser Science Conference, Baltimore, Maryland, October 4-9, 1998.

* These results were partially supported by ARO ASSERT graduate student grant of # DAAH04-96-1-0151.

4. Advanced Degrees Earned by Participating Scientific Personnel

Dana M. Calistru, Ph.D. Degree in Physics, received in summer 1997. Thesis title: "Role of local modes in nonradiative relaxation processes taking place in impurity doped laser crystals".

5. Bibliography

1. Dana M. Calistru, S. G. Demos, and R. R. Alfano, "Dynamics of local modes during nonradiative relaxation", Phys. Rev. Lett., 78, 374 (1997).
2. V. Petricevic, S. K. Gayen, and R. R. Alfano, "Laser action in Cr-activated forsterite for near-infrared excitation: is Cr^{4+} the lasing ion?", Appl. Phys. Lett. 53, 25900 (1988).
3. Dana M. Calistru, W. B. Wang, V. Petricevic, and R. R. Alfano, "Resonance Raman scattering in Cr^{4+}-doped forsterite", Phys. Rev. B51, 14980 (1995).
4. S. G. Demos, V. Petricevic, and R. R. Alfano, "Up-converted luminescence and excited-state excitation spectroscopy of Cr^{4+} ions in forsterite", Phys. Rev. B52, 987 (1995).
5. V. A. Kremerman, M. Lax, S. G. Demos, Dana M. Calistru, and R. R. Alfano, " Nonradiative energy transfer from the impurity ion into the host lattice for Cr^{4+}-doped forsterite laser crystal" , Phys. Rev. B56, 14391 (1997-II).
6. Scott Owen, S. G. Demos, Dana M. Calistru, V. Petricevic, and R. R. Alfano, "The resonance between local and phonon modes in Cr^{4+}: Ca_2GeO_4 Promotes nonradiative energy transfer", presented at the OSA 1997 Annual Meeting, Long Beach, California, October 17-21, 1997.
7. V. Petricevic, A. B. Bykov, J. M. Evans, and R. R. Alfano, Opt. Lett. 21, 1750 (1996).
8. Dana M. Calistru, S. G. Demos, Scott Owen, V. Petricevic, and R. R. Alfano, "Role of local-phonon mode coupling in the nonradiative relaxation for designing more efficient impurity doped solid state laser crystals", OSA TOPS, Vol. 10, "Advance Solid State Lasers", edited by C. R. Pollock and W. R. Bosenberg, PP 435-439 (1997).